AD-A122 213 SECONDARY ION MASS SPECTROSCOPIC STUDIES OF ELECTRODE SURFACES(U) PENNSYLVANIA STATE UNIV UNIVERSITY PARK DEPT OF CHEMISTRY N WINOGRAD AUG 82 AFOSR-TR-82-1032 1/1

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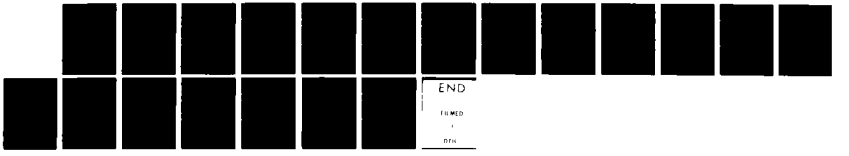

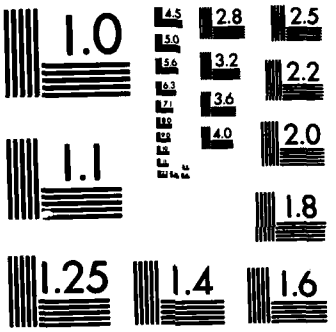

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FINAL SCIENTIFIC REPORT

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SECONDARY ION MASS SPECTROSCOPIC STUDIES OF ELECTRODE SURFACES

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I. Abstract

The major objective of this work is to develop secondary ion mass spectrometry (SIMS) and other ancilliary modern surface analysis methods as tools to elucidate electrochemical processes. The research effort is devoted both to understanding the information inherent in the surface spectroscopies and to using these methods to characterize the chemical composition of modified electrode surfaces. The SIMS results are analyzed in terms of the composition of molecular cluster ions ejected from the electrode surface. The interpretation is based on a classical dynamics model of the impact of a 1 keV ~~Ar~~ $Ar(+)$ ion into the sample. This model helps to relate the composition of these clusters to the composition of the surface. The approach should be a general one, applicable to metals, metal oxides, alloys and organic films. In short, with all of these studies we hope to demonstrate that SIMS, together with other surface spectroscopies, are powerful tools for electrochemists, providing new information relevant to corrosion processes, electrocatalysis and fuel cell technology.

II. Summary of Objectives and Accomplishments

There is currently a major interest in developing new approaches to the characterization of solid surfaces. Of particular interest has been the search for techniques capable of characterizing the rather complex state of electrode surfaces which may have been operating in an electrochemical environment such as a battery or a fuel cell. This type of information should be important in understanding the chemical factors that influence electron transfer mechanisms.

The major objective of this work has been to examine the possibility of using secondary ion mass spectrometry (SIMS) coupled with ancilliary modern surface analysis methods as tools to elucidate electrochemical processes. The research effort has been devoted both to understanding the fundamentals of the SIMS process and to applying this information to various surface characterization problems. With this technique a beam of energetic ions, usually Ar^+ ion, is directed toward the sample. The momentum dissipation that occurs following impact produces secondary ions that can be detected with a mass spectrometer. Of special interest is that the chemical composition of these fragments ought to be related to the chemical composition of the original surface. Since the fragments arise only from the top layers, SIMS is an interesting compliment to other electron spectroscopies such as Auger spectroscopy and ESCA, and to the surface analysis of electrode surfaces.

Our major effort has been to gain a fundamental understanding of the ion/solid interaction so as to glean maximum information from the spectra. This goal is being pursued from two points of view. First, in collaboration with Professor B. J. Garrison of Penn State, we have developed a classical dynamics model of the ion impact event which provides semi-quantitative information about the yields of the neutral atoms and molecular clusters that are ejected. The second approach to this problem has been to construct an angle and energy-resolved SIMS instrument which selects particles ejected from the surface in certain directions for analysis. With this instrument, the quadrupole mass spectrometer can be rotated with respect to the ion beam, to obtain scans of the yield of ions vs the polar angle, θ. By using single-crystal samples and by making energy and angle-resolved

measurements, we have made direct comparisons, for the first time, to the predictions of our theory. And, of course, with a reliable theory, we should be much more able to perform meaningful surface analysis studies using SIMS.

As a model system, we have chosen CO adsorbed onto Ni(001) into a c(2x2) or 1/2 monolayer coverage since Ni^+ ion yields are very intense from this surface and since model calculations have been recently completed. The results show excellent agreement between the calculated Ni neutral trajectories and the measured Ni^+ ion yields if the calculated values are corrected by the presence of a strong image force.

The results have a number of important implications. First, we find that the agreement between theory and experiment is only possible if the CO is bound in a linear or atop bonding configurations. This result is consistent with LEED studies and indicates that angle-resolved SIMS should be an important tool for the characterization of chemisorbed adsorbate geometries. Second, the presence of a strong image force places a number of constraints on proposed theories of the ionization mechanism in SIMS. For example, we find that the ionization probability is reasonably isotropic and independent of particle velocity. These properties virtually rule out the possibility that the ionization occurs by an Auger process as is commonly believed.

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Lectures & Travel Related to Grant

American Chemical Society Philadelphia Section Lecture, "Chemical and Structural Analysis of Surfaces by Secondary Ion Mass Spectrometry", October 20, 1980.

Clarion State College, Clarion, Pennsylvania, "Some Aspects of the Current Renaissance in Surface Chemistry", December 4, 1980.

IBM Corporation, Yorktown Heights, N.Y., "Chemical and Structural Analysis of Surface with Ion Beams", July 30, 1981.

10th Annual Surface Analysis Users Meeting, Lake Harmony, Pa, "What can SIMS tell us about solid surfaces?", September 14, 1981.

8th Annual Meeting FACSS, Philadelphia, PA., "Chemical and Structural Analysis by Secondary Ion Mass Spectrometry", September 21, 1981.

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The major objective of this work is to develop secondary ion mass spectrometry (SIMS) and other ancilliary modern surface analysis methods as tools to elucidate electrochemical processes. The research effort is devoted both to understanding the information inherent in the surface spectrocopies and to using these methods to characterize the chemical composition of modified electrode surfaces. The SIMS results are analyzed in terms of the composition of molecular cluster ions ejected from the electrode surface. The interpretation is based on a classical dynamics model of the impact of a 1 keV Ar^+ ion into the sample. The model helps to relate the composition of these clusters to the composition of the surface. The approach should be a general one, applicable to metals, metal oxides, alloys and organic films. In short, with all of these studies we hope to demonstrate that SIMS, together with other surface spectroscopies, are powerful tools for electrochemists, providing new information relevant to corrosion processes, electrocatalysis and fuel cell technology.